

Saimaa University of Applied Sciences
Technology, Imatra
Degree Programme in Paper Technology
Specialization in Paper Technology

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COATING, TITANIUM DIOXIDE AND SOLAR CELL

Bachelor's Thesis 2011

ABSTRACT

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Coating, Titanium Dioxide and Solar Cell, 48 pages

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The objective of this bachelor's thesis is to get basic ideas about coating and a deep understanding of properties of titanium dioxide pigments as well as their application and performance in solar electricity energy technology. This thesis consists of three main parts, eight chapters.

The first part is about basic knowledge of coating and tests of coated paper. Coating pigments are generally introduced in the part.

In the second part, coating additives are introduced in details from two aspects – optical brightening agents and titanium dioxide. Especially properties of titanium dioxide are introduced here.

The last part is about the solar cell. The key point for this part is about the new type of solar cell which is based on dye-sensitized nanocrystalline titanium dioxide.

Keywords: Coating, Optical Brightening Agents, Titanium Dioxide, Coating Pigments, Smart Material, Dye-sensitized Solar Cell, Titanium Dioxide Dyed Solar Cell

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LIST OF SYMBOLS

OBA – optical brightening agents

UV – ultraviolet

ISO – International Organization for Standards

CIE – the International Commission on Illumination

TiO₂ – titanium dioxide

PV – photovoltaic

CWSN – critical wax strength number

a-Si – amorphous silicon

CdTe – cadmium telluride

CIGS – copper indium gallium diselenide

DSSC – dye-sensitized solar cell

a-Si – amorphous silicon

CIGS – copper indium gallium diselenide

e⁻ – electron

γ – the value of paper measured under conditions C/2°

γ₀ – the γ value of a single sheet measured under the same conditions (with same geometry) against a black backing

F – the reflectivity of the coating

np – the reflectivity of the coating

nr – the refractive index of the binder in which the pigment is incorporated

1 INTRODUCTION

Pigment coating provides paper and paperboard enhanced smoothness, better ink receptivity, more whiteness, and more gloss (Kocurek 1990, 4). As the most important white pigment currently produced commercially and the most expensive coating pigments used in paper industry, titanium dioxide pigments have many requirements which an ideal pigment needs (Gullichsen 2000).

For balancing the mismatch of supply and demand of energy, sustainable and renewable generation of energy/electricity by photovoltaic systems has been developed. Storage of energy is often essential for these systems to become a competing technology for the conventional energy generation. One way to solve the problem of storage is the development of photochemical systems that use sunlight (photons) directly to drive reversible chemical reactions leading to products that can be used for energy storage. (Sommeling, et al., 2008., Halme 2002)

Titanium dioxide is not widely used in paper industry only, because of its flexible manufacturing process, low manufacturing cost, high efficiency, low manufacturing cost and long term stability etc., it is also in a growing number of applications in solar cell. A new type of solar cell which is based on dye-sensitized nanocrystalline titanium dioxide has been developed. (Sommeling & Späth 2008.)

2 PIGMENT COATING

2.1 Objective of Coating

Coating improves the printing properties of paper; it provides the printer with a sheet with a superior surface for printing (Kocurek 1990, 4). Pigment coating provides enhanced smoothness, better ink receptivity, more whiteness, and more gloss. Thus, quality printed papers and boards are coated. (Gullichsen 2000, 14.) Coating does not cover imperfections in the underlying paper, but it makes them more noticeable. (Kocurek 1990, 12).

2.2 Coating Pigments

2.2.1 Functions of Coating Pigments

Pigment is the most abundant component in coating. Thus, pigment is naturally the most essential factor affecting the properties of coating. And the volume fraction is important. The smaller the particle size is, the glossier will be the coating. (Gullichsen 2000, 14-17.)

2.2.2 Ideal Pigment

Every particle must be clusters separated and wetted for obtaining the maximum benefit from any pigment. When choosing a certain type or types of coating pigment, the smaller the particle size is, the glossier will be the coating. However, not only will large aggregates make the coating rough, in some special cases, they will break down under supercalendering and cause dusting. (Lewis 1988, 1-8.)

2.2.3 Pigment Properties

If an ideal pigment existed, it would have the following properties:

- Good chemical stability and low solubility in water
- Good brightness (Good light reflectivity)
- Free from impurities
- Appropriate particle size and proper particle size distribution
- Good opacity (High refractive index)
- Small binder demand
- Good flow properties as an aqueous suspension
- Good dispersability
- Good glossing properties
- Outstanding compatibility with other coating components
- Low density
- Non-abrasive
- Low water absorption
- Cheap

Of course different pigments have different combinations of these properties, there is no pigment could have all. Titanium dioxide has many of them. (Gullichsen 2000, 61.)

2.2.4 Classification of Pigments

Pigments could be classified in lots of ways. A commonly used way is to classify pigments in the following way:

- Main pigments
- Special pigments
- Additional pigments

Main pigments are those pigments which form the major fraction of the pigment part of a coating colour. Special pigments are similar to main pigments except their limited applications. Pigments that form the minor fraction of the pigment part of a coating colour belong in the class of additional pigments. Titanium dioxide is a commonly used additional pigment. (Gullichsen 2000, 62.)

2.3 Testing of Pigment Coated Papers

The coated surface of paper must be of such quality that it is optically acceptable, ink-receptive and durable for the carrier for images that will be received during printing. Thus, brightness, opacity, smoothness, gloss, ink receptivity, and surface strength are important for pigment coated paper. (Kocurek 1990, 15.)

2.3.1 Brightness

In pigment coated paper, the coating paper grade structure is based primarily on brightness. Because the brightness of pigment coated paper depends heavily on the brightness of raw stock, the raw stock should have a brightness which is very close to that of the dry coating in practice. (Kocurek 1990, 15.)

Brightness is an intrinsic reflectance factor, which is determined with a brightness meter whose sensitivity to light agrees with ISO standard 2470. (Gullichsen 1999, 173.)

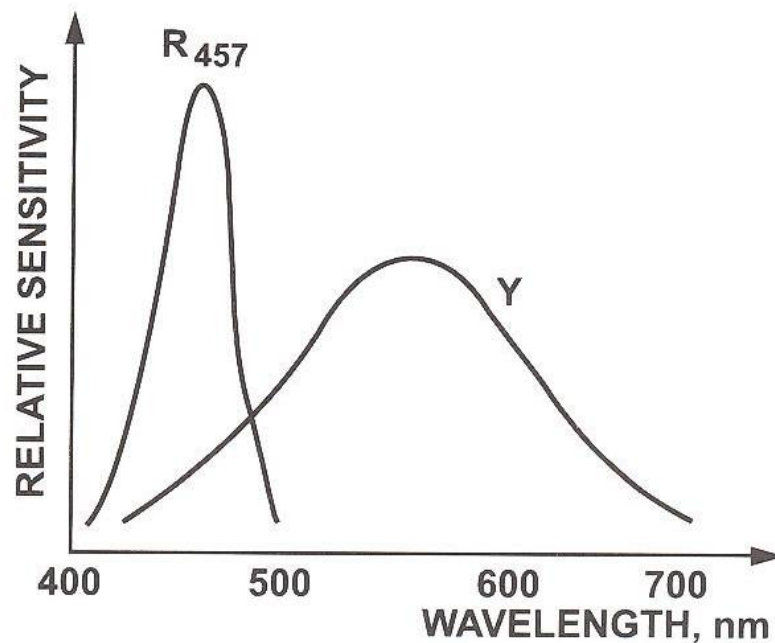


Figure 2.1 Sensitivity distribution of ISO brightness and Y-value (Gullichsen 1999)

Figure 2.1 shows the sensitivity spectrum. The peak of the sensitivity spectrum corresponds to the wavelength of 457 nm. This means the origin of the abbreviation R₄₅₇. (Gullichsen 1999, 173.)

There are two standards for brightness from TAPPI: T 525 – Pulp (diffuse illumination and 0° observation) is identical to ISO 2470. And T 452 – Pulp, paper and paperboard (directional reflectance at 457 nm) is identical to different geometry. (Gullichsen 1999, 173, 174.)

The American paper industry uses the standard brightness instrument which has 45° illumination and 0° viewing. According to the test method TAPPI T 452, the

measurement is through a 457 nm filter and is based on the reflectance of magnesium oxide as being 100%. (Kocurek 1990, 15.)

2.3.2 Opacity

Opacity is defined as the measure of a material's ability to obstruct the passage of light. When no light is transmitted the opacity is 100%. (Kocurek 1990, 15.)

There are two commonly used methods to determine opacity:

$$\text{Opacity, \%} = (1 - \gamma_0 / \gamma) 100 \quad (1)$$

Where:

γ is the value of paper measured under conditions C/2°.

γ_0 is the γ value of a single sheet measured under the same conditions (with same geometry) against a black backing.

The determination is described by standard methods ISO 2471, SCAN-P 8 and TAPPI T 519. (Gullichsen 1999,175.)

In practice, the opacity is usually given by a value which is known as the contrast ratio, which is the ratio of the diffuse reflectance from a same sheet of paper backed by a black body to the reflectance backed by a white body but the same area. The contrast ratio is an indirect measurement which measures the amount of transmitted light. (Kocurek 1990, 15)

$$\text{Contrast Ratio} = \text{Opacity (89\% reflectance backing)}, \% = (R_0 / R_{0.89}) 100 \quad (2)$$

Where:

R_0 is the reflectance factor measured against a black backing under standard conditions.

$R_{0.89}$ is the reflectance factor of the same sheet measured against a backing with a reflectance of 89%.

There is difference between these two opacity determination methods. The devices which are used for measurements represent different measurement geometries and illuminants. Thus, the results are not comparable. (Gullichsen 1999, 175.)

2.3.3 Smoothness

The principle reason for pigment coating is to produce paper a smooth surface which can ensure good contact between the coated paper and the printing plate. An irregular or rough surface with many discontinuities cannot receive a satisfying impression. (Kocurek 1990, 15.) The purpose of smoothness measurement is to find a figure describing the topography of the paper surface simply (Gullichsen 1999, 156).

Smoothness is determined by the rate of airflow between a sheet of paper and a plane surface in contact with the paper. The rate of flow between the two surfaces is proportional to the volume of air voids.

TAPPI Method T 479 is used to test of smoothness with the Bekk instrument. Bendtsen and Sheffield smoothness tests are used with TAPPI Useful Methods 535 and 518, respectively. (Gullichsen 1999, 15.)

2.3.4 Gloss

Gloss is the attribute of a surface which makes the object look shiny or lustrous, and it is a measure of the degree to which a coated surface approaches a perfect specular surface or mirror in its ability to reflect light (Gullichsen 1999, 16). Gloss is affected by specular reflection from the surfaces. Gloss values of pigment coated paper fall with broad range. High gloss is desired in a high quality, prestigious printed image. Gullichsen 1999, 164.)

There are different gloss measurement methods for measuring different aspects of the phenomenon. The gloss of papers and paperboards vary widely, so two measurement methods are necessary. TAPPI Methods T 480 and T 653 are used in gloss tests. (Gullichsen 1999, 164.)

The specular angle refers to incident and viewing angles measured from the perpendicular plane of the surface; it is selected by experiments that showed the best correlation with visual ranking at this angle. TAPPI T 480 uses a 75°angle, and TAPPI T 653 uses a 20°angle. TAPPI T 653 is used for evaluation of high-gloss papers and boards such as lacquered papers and cast-coated papers. (Gullichsen 1999, 164)

2.3.5 Ink Receptivity

Printing ink acceptance of paper will be improved significantly when pigment coating is applied to raw stock.

TAPPI Useful Method 553 is used to test ink receptivity. K&N test from TAPPI Useful Method 553 is applied, to the coated surface is used a special ink containing an oil-soluble dye dissolved in a nondrying varnish, which allows the ink to penetrate for a set time and the excess is the wiped off.

The reflectance of the ink surface measures the ink receptivity. The higher the ink receptivity is, the lower the reflectance value will be. (Gullichsen 2000, 16.)

2.3.6 Surface Strength

Surface strength is defined as the ability of the paper to resist a force pulling out fibers or fiber bundles from its surface. A low surface strength may make linting problems and destroy the printing result or cause runnability problems. (Gullichsen 1999, 148.)

Methods for surface strength testing of paper usually use high viscosity, tacky oils or printing inks. A commonly used tester is the one developed by IGT and described in ISO 3738. This unit prints the paper using very tacky oil, at a continuously rising speed. The printing speed at the picking of the surface begins is measured. The viscosity of the oil and the product of the speed is a measure of the surface strength of the paper. (Gullichsen 1999, 149, 150)

Another test method is the Dennison wax pick test, TAPPI T 459. In this test, sealing wax sticks with different picking strength values are fastened on paper by melting. The wax number, at which the paper surface does not yet break when removing the wax piece, indicates the surface strength. The critical wax strength number (CWSN), which is the numerical surface strength value. (Gullichsen 1999, 149, 150.)

The resistance, with the coating is to be picked or pulled off the raw stock during printing, is determined by pick strength. The printing quality will be poor when picking of the coating surface occurs. Pick strength is determined by the amount of binder present. (Gullichsen 2000, 16.)

3 COATING ADDITIVES

3.1 Optical Brightening Agents

Additional pigments improve printing properties. The application of additional pigments leads to improvement of optical properties, gloss, and ink absorption.

The brightness of paper and board has grown stunning during the recent years. The brightness of pulp, fillers and coating pigments is not high enough to reach the brightness targets. Thus, there is a need to use optical brightening agents (OBA). (Gullichsen 2000, 298.)

3.1.1 Fluorescence and Chemical Structure

“Fluorescence is a phenomenon where the molecules of a fluorescent substance become electronically excited by absorbing light energy and then emit this energy at a higher wavelength. Fluorescence is usually restricted to compounds with large conjugated systems containing π -electrons. Most of the OBAs on the market are derivatives of bis (triazinylamino) stilbene.” (Gullichsen 2000, 298.)

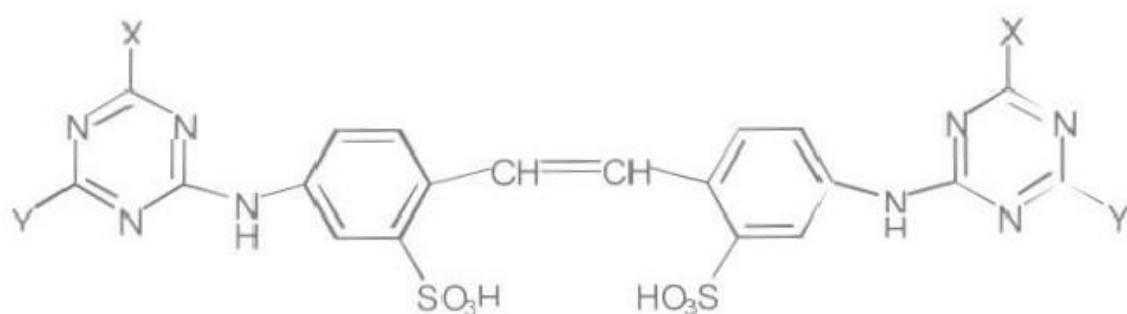


Figure 3.1 Structural formula of bis (triazinylamino) stilbene (Gullichsen 2000, 299)

The strong fluorescence is only exhibited in the trans-isomer. Properties like substantivity and solubility are influenced by the nature of X and Y.

The OBAs used in paper industry are water-soluble because they are Na-salts.

OBAs absorb ultraviolet radiant energy at 300-360 nm and re-emit the energy in the visible range mainly in the blue wavelength region. This results in higher brightness or whiteness by increasing the amount of light emitted. And bluish reflected light results in the compensation of yellow shade of paper, contributing to making whiter look of paper. (Gullichsen 2000, 299.).

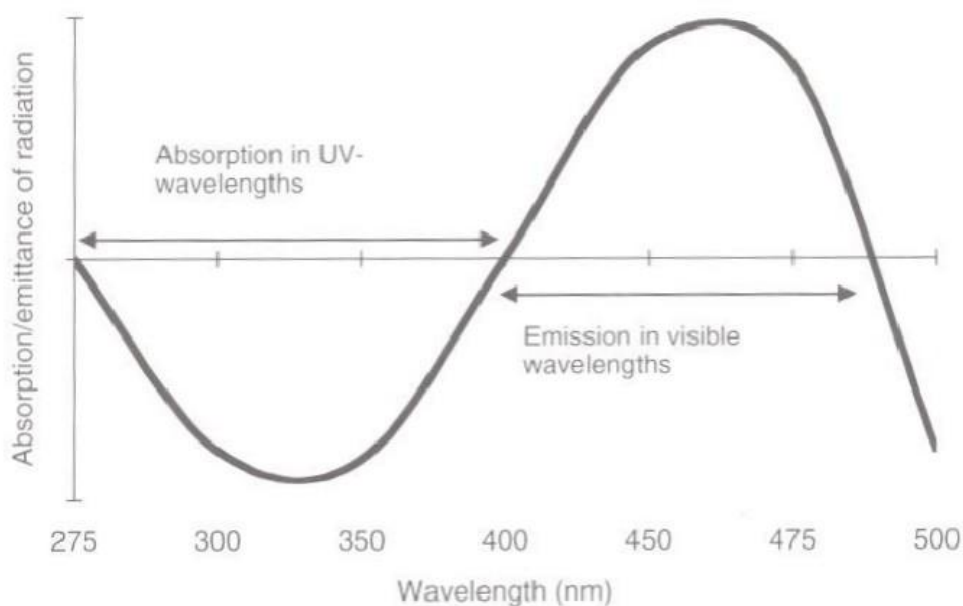


Figure 3.2 Functioning mechanism of OBA in paper coatings (Gullichsen 2000, 299)

Whiteness is the degree to which a surface is white; it is defined as the reflectance of light across the visible spectrum including colour components in the measurement. Brightness again is an attribute of visual perception in which a source appears to be radiating or reflecting light. It is defined as the relectance of light at the wavelength of 457 nm without colour in the measurement. (Gullichsen 2000, 299.)

Instead of the traditional ISO brightness which does not define the illuminant for use in the determination, to measure the brightness or whiteness of paper and board containing OBAs, the test method used more and more is the CIE whiteness, which requires an instrument having a known amount of UV in the illumination. (Gullichsen 2000, 299.)

3.1.2 Types of OBA

Based on the stilbene molecule described in Fig 3.1, there are differences between the number of solubilizing sulfonic groups. The differences of the optical brighteners are divided to disulfonated OBAs, tetrasulfonated OBAs and hexasulfonated OBAs. (Gullichsen 2000, 299.)

Disulfonated OBAs have two sulfonic groups and very good affinities, they are mostly used in the wet end. But this OBA has limited solubility.

Tetrasulfonated OBAs are the most commonly used. They have medium affinity and good solubility. They can be mostly applied in wet end, size-press and coating in paper industry.

Hexasulfonated OBAs can be added up to 15% of pigment amount since they are very soluble. They are specialties used in coatings where high brightness is required. (Gullichsen 2000, 295.)

3.1.3 The Role of Carrier

A good carrier needs to be linear and contain hydroxyl or other hydrophilic groups. OBAs work only when they are fixed to a carrier. (Gullichsen 2000, 300.)

The contact between the carrier and OBA is increased by linearity, so physical bonds can be formed between the OBA and hydrophilic groups of the carrier. (Gullichsen 2000, 300.)

UV exposure causes yellowing of brightened paper, but a good carrier increases the light stability, so the yellowing of paper might be compensated. Furthermore the carrier influence the migration of OBA; it works better in against the migration when the carrier is more efficient. (Gullichsen 2000, 299.)

3.2 Titanium Dioxide

3.2.1 Introduction of Titanium Dioxide

Titanium dioxide is the ninth most abundant element in the earth's crust, it is the most important white pigment currently produced commercially (Gullichsen 2000, 121).

"Pure titanium dioxide (TiO_2) is a colourless crystalline solid. As with other d-block elements in its group of the Periodic Table, TiO_2 is stable, nonvolatile, largely insoluble, and rendered refractory by strong ignition. " (Lewis 1988, 17.)

TiO_2 pigments are one of the most expensive pigments used in paper industry (Gullichsen 2000, 121). They are synthetic pigments produced by expensive raw materials and complicated process (Lewis 1988, 1).

3.2.2 Properties of Titanium Dioxide Pigments

Titanium dioxide pigments have extremely high refractive indices, whiteness, and high reflectance in the visible region of light and optimal particle size. These

properties make them the most efficient white pigments.

Titanium dioxide is the most stable white pigment; due to its stability, titanium dioxide is non-toxic and considered to be a very safe material.

There are two forms of titanium dioxide pigments: rutile and anatase.
(Gullichsen 2000, 125.)

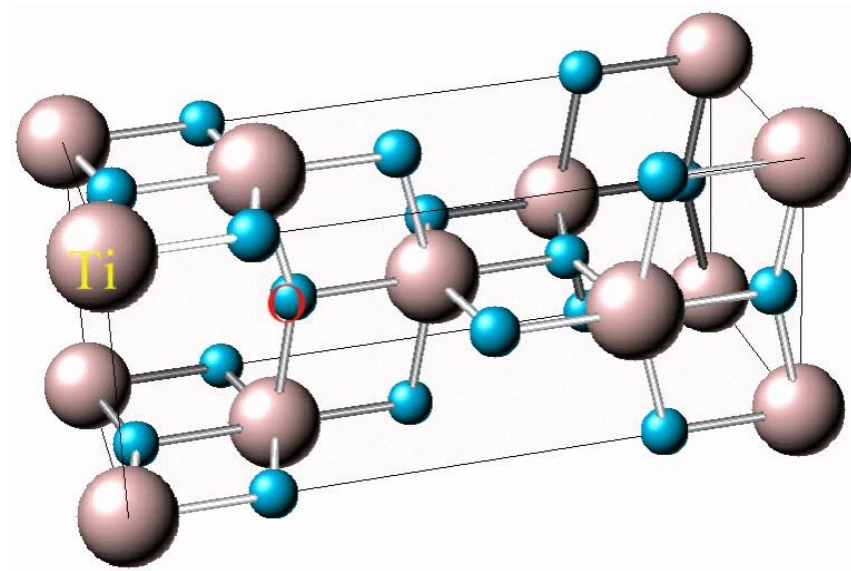


Figure 3.3 Crystal structure of anatase titanium dioxide.

(<http://cst-www.nrl.navy.mil/users/sullivan/TiO2/tio2.html>)

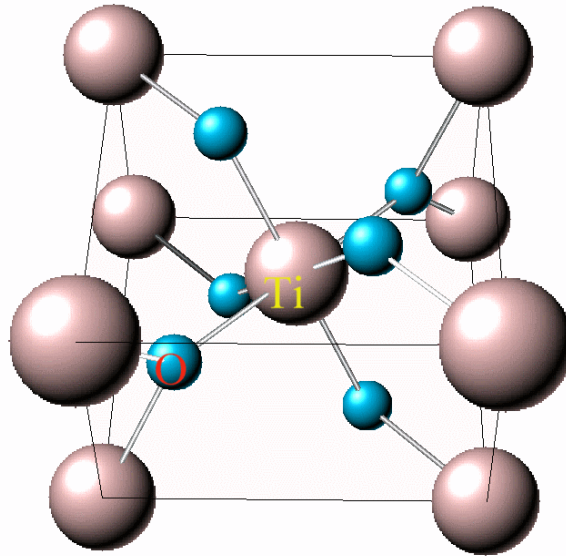


Figure 3.4 Crystal structure of rutile titanium dioxide.

(<http://cst-www.nrl.navy.mil/users/sullivan/TiO2/tio2.html>)

Anatase pigment has a less compact crystal structure than rutile pigment, which is the reason for its lower refractive index, less stability and lower density. (Gullichsen 2000, 125.)

3.2.3 Opacity

The most essential property of white pigment is its ability to opacify and whiten the medium in which it is dispersed. The opacifying potential is controlled by two properties ---- refractive index and particle size. Rutile titanium dioxide has the highest refractive index of all the available white pigments. This property gives titanium dioxide the greatest possible opacifying potential. (Lewis 1988, 15-18.)

Refractive index is not a fixed property but varies with the wavelength of light, as illustrated in Figure 3.5:

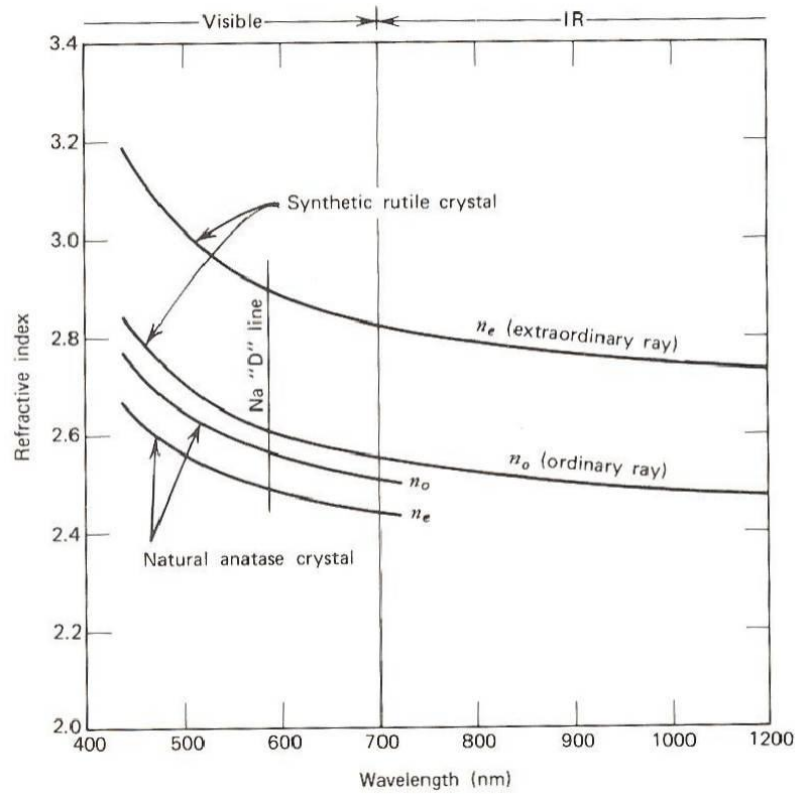


Figure 3.5 Refractive indices of synthetic rutile crystal and natural anatase crystal as a function of wavelength (Lewis 1988, 17)

An indication of the influence of refractive index on opacity can be achieved by Fresnel equation:

$$F = \frac{(np - nr)^2}{(np + nr)^2} \quad (3)$$

Where F is the reflectivity of the coating, np is the refractive index of the pigment, nr is the refractive index of the binder in which the pigment is incorporated. By this equation, an indication of the potential opacity of a series of pigments can be calculated. (Lewis 1988, 17.)

3.2.4 Colour

Two aspects of colour are important to the users of titanium dioxide pigments---whiteness and undertone.

Whiteness is the impression produced when the principal colouring matter is the white pigment itself; it is enhanced by careful purification of the pigment during the manufacturing process, and it is particularly important to reduce the concentration of contaminant elements with coloured oxides to a minimum. (Lewis 1988, 20.)

Undertone is defined as the colour obtained when such a pigment is greatly extended with white, it is usually applied to coloured pigments. The undertone of a white pigment is the hue of a gray paint containing the pigment in admixture with a standard black pigment. Undertone is dependent on the particle size of the titanium dioxide mostly, thus it can be controlled by manufacturer. (Lewis 1988, 20.)

3.2.5 Gloss

According to Lewis (1988, 21) gloss is a sensation experienced by an observer when light is reflected from a surface; it is an essential parameter in surface coating. Gloss is influenced by the distribution and concentration of titanium dioxide pigments in the paint film. When the paint film is optically smooth, its specular gloss will be directly related to the refractive index of the film surface; however, paint films generally have a degree of surface roughness. The surface roughness can be considered to consist of two components-macro roughness and micro roughness. The result for macro roughness of surface defects is of the order of 1 μm or more in height; micro roughness is attributable to defects of the order of 0.6 μm or less. Thus, it is primarily micro roughness which is affected by

the presence of titanium dioxide pigment particles at or near the surface of the paint. (Lewis 1988, 21.)

The primary reason for incorporating titanium dioxide pigment in paint films is producing opacity. However, increasing the level of pigmentation to achieve high opacity also causes decrease of the observed gloss. In the case of latex paints, where no such clear layer exists, the initial observed gloss values are lower and tend to fall as pigmentation rise, although it is predicted that increasing the refractive index of a paint film will increase the observed gloss value theoretically. The reason is, as the pigment loading increases, the presence of pigment particles near the surface of the film causes a marked increase in surface micro roughness, thus, observed gloss decreases. (Lewis 1988, 22.)

3.2.6 Dispersibility

To obtain the maximum benefit from any pigment, every particle must be wetted and clusters of particles separated. Because large aggregates make the coating rough and cannot be bonded properly to the base stock; in extreme cases, they will break down under supercalendering and cause dusting. (Kocurek 1990, 18.)

In relative terms, titanium dioxide pigments are easily dispersible. As a result of surface treatment, titanium dioxide can be processed using a wide variety of modern machinery and provide correct mill-base formulating procedures have been followed. (Lewis 1988, 24, 25.)

There are agglomerates which need energy to be dispersed in water in dried titanium dioxide pigments. Several types of dispersion equipment can be used successfully to prepare titanium dioxide dispersions. (Lewis 1988, 24-27.)

Commonly, titanium dioxide pigments are dispersed by various amounts of

sodium polyacrylate. Instead of sodium polyacrylate, other dispersing agents such as special polyacrylate (mixed salt of an acrylic polymer) or amino alcohols should be used, for dispersing uncoated rutile and anatase. (Gullichsen 2000, 129.)

3.2.7 Electrical Properties

Pure titanium dioxide is a semiconductor, which means its electrical conductivity is very low (approximately $10^{-10} - 10^{-13}$ S/cm). Thus, pure titanium dioxide can be considered as an insulator. However, if conductivity increases by a factor of 10^7 over the temperature range 30-420°C, conductivity will also rise if reduction occurs to produce Ti^{3+} ions within the Ti^{4+} crystal lattice.

Details of the electrical properties of titanium dioxide are shown in table 3.1, including average dielectric constants valid for polycrystalline solids, which the crystallites are freely oriented. (Lewis 1988, 26, 27.)

Table 3.1 Selected electrical properties of titanium dioxide (Lewis 1988)

<i>Property</i>	<i>Rutile</i>	<i>Anatase</i>
Dielectric constant, pigment	114	48
Single crystal		
<i>a</i> Direction	170	
<i>c</i> Direction	86	
Loss tangent		
<i>a</i> Direction	1.1×10^{-2} – 2.0×10^{-4}	
<i>c</i> Direction	3.5×10^{-1} – 1.6×10^{-2}	
Electrical conductivity (single crystal S/cm)		
<i>a</i> Direction		
30°C	1×10^{-10}	
227°C	1×10^{-7}	
<i>c</i> Direction		
30°C	1×10^{-13}	
227°C	1×10^{-6}	
Breakdown voltage (V/mil)	600–700	
Dipole moment (debye)	2.8–3.3	
Magnetic susceptibility	$(7.8\text{--}8.9) \times 10^{-8}$	

^a After Kampfer (1973).

Since the high dielectric constant of titanium dioxide and other titanium compounds, the electrical properties of rutile titanium dioxide are important in certain plastics and ceramics applications, to advantage in the manufacture of electrical condensers and other electronic components. (Gullichsen 2000, 128.)

4 APPLICATIONS

4.1 Applications of Titanium Dioxide

Titanium dioxide has a wide range of applications. Although a general indication of titanium dioxide pigments has already been given, each individual consumer industry has specific requirements. (Lewis 1988, 32.)

4.1.1 Paper

In paper industry, about 14% of titanium dioxide pigments are used in paper industry as filler or coating pigments (Gullichsen 2000, 128). Titanium dioxide pigments are used as a direct beater addition to pigment the paper stock and in the manufacture of coatings (Lewis 1988, 39).

The main function of titanium dioxide in paper applications is to increase the opacity and brightness of the final product, but it will have an effect on the mechanical properties of the sheet. Parameters such as burst and tensile strength are affected by filler content; (Lewis 1988, 39) which means increasing the amount of titanium dioxide pigment in a paper will cause a progressive decrease in strength. However, as titanium dioxide is always used in conjunction with big amounts of clay, its influence on the mechanical properties of sheet can be ignored. (Gullichsen 2000, 128.)

For direct beater addition, uncoated anatase pigments are widely used; because uncoated anatase pigments are self-dispersing in water and cost less than their rutile equivalents. (Lewis 1988, 39.)

Both anatase and rutile pigments are used in the manufacture of paper coatings,

which are delivered as a high- solids (> 65%) slurry. Application of a coating to the paper surface improves the printing properties of an otherwise variable substrate. When optical brighteners are used in the paper coating, anatase grades must be employed because of the high UV absorption characteristics of rutile pigments. (Lewis 1988, 39.; Gullichsen 2000, 128.)

In paper industry, a highly specialized application is the manufacture of paper laminates. For such systems, the main requirement of pigments is a high resistance to discolouration, which is caused by partial reduction of titanium to its trivalent state, in the presence of UV radiation and the melamine resin used to impregnate the paper. Rutile pigments are preferred for such applications generally, but they require a secondary heat treatment or a highly specialized surface treatment to give a satisfactory level of performance. (Lewis 1988, 39.)

4.1.2 Plastic and Rubber

Titanium dioxide pigments are principally used in plastics to impart whiteness and opacity. Dispersibility is an important pigmentary property in many plastic systems. Satisfactory levels of dispersion can more readily be achieved by employing siliconetreated pigments for certain application areas. (Lewis 1988, 38.)

Today, titanium dioxide plastic is a new photovoltaic material. The driving force for the development of researching for new photovoltaic materials for solar cell is the reduction of the cost of photovoltaic cells and modules. (Halme, 2002.)

4.1.3 Solar Cell

As the properties of good light absorption and stability, titanium dioxide has been developed in making solar cell that is based on dye-sensitized nanocrystalline titanium dioxide. Chapters 5.4 and 6 will introduce applications of titanium dioxide pigments in solar cell industry in detail.

5 SOLAR CELL

5.1 Introduction

Sustainable and renewable generation of energy/electricity by photovoltaic systems is being developing because the mismatch of supply and demand of energy. Storage of energy is often essential for these systems to become a competing technology for the conventional energy generation. One way to solve the problem of storage is the development of photochemical systems that use sunlight (photons) directly to drive reversible chemical reactions leading to products that can be used for energy storage. (de Boer 2011)

Solar electricity energy technology is growing steadily nowadays. Producing electricity directly from solar radiation is near to an ideal way to use natural renewable energy. Developing more economical material for making solar cell is an essential topic today.

5.1.1 What is Solar Cell

Solar cell is also called photovoltaic cell or photoelectric cell; it is a solid state device which converts the energy of sunlight directly into electricity by the photovoltaic effect. (http://en.wikipedia.org/wiki/Solar_cell)

Some cells are designed to efficiently convert wavelengths of solar light which reach the Earth surface. However, other solar cells are optimized for light absorption beyond Earth's atmosphere. (Sommeling, et al., 2008.)

The oldest photovoltaic cell is the photoelectrochemical solar cell, for this solar cell a semiconductor-electrolyte junction is used as a photoactive layer. Energy

conversion efficiencies exceeding 16% have been achieved with the photoelectrochemical solar cells utilizing semiconductor photoelectrodes (Meissner 1999), these solar cells have been left without practical importance because of instability by photocorrosion. (Halme 2002).

A new type of solar cell which is based on dye-sensitized nanocrystalline titanium dioxide has been developed by M. Grätzel and coworkers (O' Regan and Grätzel 1991; Nazeeruddin, et al. 1993). Remarkably high quantum efficiencies have been reported for this type of solar cell (also called nc-DSC), with overall conversion efficiencies up to 11 %. (Green, et al. 1998.)

5.1.2 Cost of Solar Electricity

Power generation by grid connected PV systems might be the main application today, and it is pursued to be realized in the future in a large scale. Thus, the cost of PV system needs to be reduced significantly; which means the cost of solar electricity needs to be reduced. (Halme 2002.)

There are two ways to reduce the cost of PV system: improvement of performance (efficiency) and reduction of direct manufacturing cost. With this respect, two requirements are needed: high efficiency and low manufacturing cost. (Halme 2002.)

5.2 Different Solar Cells

There are different solar cells. They are single-crystal and polycrystalline silicon solar cell; Thin film solar cell; III-V Semiconductors and Photoelectrochemical solar cells.

5.2.1 Single-crystal and Polycrystalline Silicon Solar Cell

The first silicon solar cell was developed by Chapin, Fuller and Pearson at the Bell Telephone Laboratories in the mid 1950's. There was already about 6% efficiency for the first silicon solar cell (Kazmerski 1997). The silicon solar cells occupy 82% of the photovoltaic market today and the record efficiency for a laboratory cell is 24.7% (Green 2001). The efficiency of the commercial crystalline silicon solar panels is the best which occupies about 15% (Shah et al. 1999).

Because of the high quality Si has been produced at large quantities by the semiconductor industry, Si dominates the PV market. The processing of crystalline silicon wafers is high-level semiconductor technology, and it is very capital intensive and expensive. And this cost is added directly to the cost of the photovoltaic modules. So the cost of processed silicon wafers contribute to fifty per cent of the total manufacturing cost of the module. (Goetzberger & Hebling 2000.)

There is a big question for the Si photovoltaic technology - the availability of highly purified Si. The PV industry has been using mainly low cost reject material from the semiconductor industry. This gives a problematic dependence on the volatile semiconductor market which causes fluctuations and also the problem of the cost of Si material for the solar cells. It is generally seen that the dominance of the standard Si PV technology in the growing PV market can be realized only

by production of special solar cell grade silicon actually. However, because of the high purity requirements and the small market for the special silicon, the first efforts to produce such material have been unsuccessful at the moment. (Goetzberger & Hebling 2000.)

While the crystalline silicon technology is relatively mature, there is still a large potential of cost reduction. However, the cost reduction can be achieved only by increasing manufacturing volume. In manufacturers' opinion, this is coupled to the need for the special solar cell grade silicon supply and from the market's point of view not very easy to achieve at 20 percent PV system costs without governmental subsidies for customers to create artificial markets for the solar electricity. (Goetzberger & Hebling 2001.)

5.2.2 Thin Film Solar Cell

The crystalline silicon is normally referred to as the first generation photovoltaic technology. The second generation photovoltaic consists of thin film solar cell materials such as cadmium telluride (CdTe), amorphous silicon (a-Si), copper indium gallium diselenide (CIGS), and thin film crystalline silicon. (Green 2001.)

The thin film solar cells have been developed because of their potential for the reduction of manufacturing costs. While silicon solar panels are assembled from individual cells process starts from about 100 cm² silicon wafers, while thin film semiconductor materials can be deposited onto large surfaces, which is beneficial for volume production. (Green 2000b.)

The thin film semiconductor materials have much higher absorption coefficient than silicon also, as the direct band gap semiconductors, and therefore typically less than 1 mm thick semiconductor layer is required, which is 100-1000 times

less than for Si. Thus, the cost of semiconductor material is reduced, more expensive semiconductors can be used in the thin films. (Goetzberger & Hebling 2000.)

5.2.3 III-V Semiconductors

Semiconductors such as GaAs, GaAlAs, GaInAsP, InAs, InSb, and InP are interesting solar cell materials. They have near-optimal band gaps and are extremely expensive. These materials have been only found applications in the space solar cells. So the performance of III-V Semiconductors is more important criterion than their costs. And to some extent in concentrating systems where the active surface area of the cells can be reduced significantly, thus, expensive materials can be used. (Halme 2002.)

5.2.4 Photoelectrochemical Solar Cells

Photoelectrochemical solar cell is the oldest type of photovoltaic cell, which was used already by Becquerel for the discovery of the photovoltaic effect in 1839. A semiconductor-electrolyte junction is used as a photoactive layer in the photoelectrochemical solar cell. While energy conversion efficiencies exceeding 16% have been achieved with the photoelectrochemical solar cells utilizing semiconductor photoelectrodes, instability by photocorrosion makes them have no practical importance. Furthermore, the photoelectrochemical solar cells using same semiconductor materials as in the commercial solar cells, such as Si, CuInSe₂ or GaAs do not offer any real advantages over the established solid state solar cells. (Meissner 1999.)

5.3 Materials of Solar Cells

Materials for efficient solar cells must have characteristics match to the spectrum of available light. Light absorbing materials can often be used in multiple physical configurations to take advantage of different light absorption and charge separation mechanisms. (Sommeling, et al., 2001, 1.)

5.4 Titanium Dioxide Solar Cell

As Sommeling and Späth (2008) point out titanium dioxide solar cell has the potential to reach low costs in future outdoor power applications; it is the solar cell which is based on dye-sensitized nanocrystalline titanium dioxide.

The application of titanium dioxide solar cell requires only a low power output, since this is easier to achieve. Less stringent efficiency requirements of titanium dioxide solar cell make the manufacturing process more flexible, i.e. the requirements for materials used are less severe.

Lower manufacturing costs and more flexibility in manufacturing process open the way for alternative production processes. (Sommeling & Späth 2008.)

6 WORKING PRINCIPLE OF TiO_2 SOLAR CELL

Titanium dioxide, which is sensitized for visible light by a monolayer of adsorbed dye, works as a bandgap semiconductor. The most frequently used dye is, for reasons of best efficiencies, cis-(NCS)2bis(4,4'-dicarboxy-2,2'-bipyridine)-ruthenium(II). The photoelectrode in such a device consists of a nanoporous TiO_2 film (approx. $10\mu\text{m}$ thick) deposited on a layer of transparent conducting oxide (TCO, usually $\text{SnO}_2:\text{F}$) on glass or plastic, as can be seen in figure 6.1.

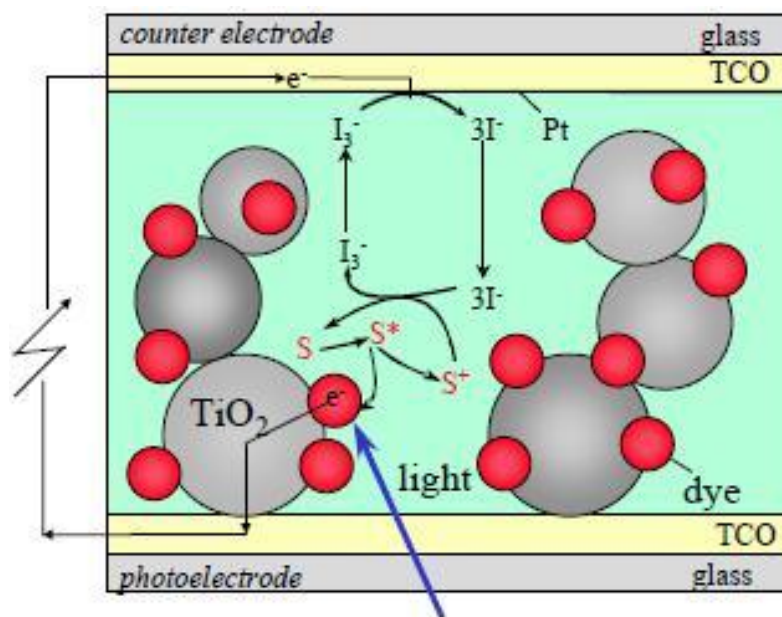


Figure 6.1 Working Principle of TiO_2 Solar Cell (Sommeling & Späth 2008)

Photo and counter electrode are clamped together in a complete cell, and the space between the electrodes and the voids between the titanium dioxide particles are filled with an electrolyte which consists of an organic solvent containing a redox couple; the electrolyte is usually iodide /triiodide (I^-/I_3^-). (Sommeling & Späth 2008.)

Less than 1 % of the incoming light (one sun conditions) is absorbed by a dye monolayer on a flat surface. To obtain reasonable efficiencies comparable to established solar cell technologies, the surface area is enlarged by a factor of 1000, by using nanoparticles of TiO₂ with a diameter of approximately 10-20 nm. (Sommeling & Späth 2008.)

The working principle of the titanium dioxide solar cell is based on excitation of the dye followed by fast electron injection into the conduction band of the TiO₂, leaving an oxidized dye molecule on the TiO₂ surface. Injected electrons percolate through the TiO₂, and then they are fed into the external circuit. At the counter electrode, triiodide is reduced to iodide by metallic platinum under uptake of electrons from the external circuit:



Iodide is transported through the electrolyte towards the photoelectrode, where it reduces the oxidized dye. After this process, the dye molecule is ready for the next excitation/oxidation/reduction cycle. (Sommeling & Späth 2008.)

6.1 Theoretical Issue of TiO₂ Dye Cell Operation

The operation of a photovoltaic cell can be generally divided into three basic steps:

- Light absorption
- Charge separation
- Charge collection

6.1.1 Light Absorption

While the high efficiency of the dye sensitized solar cell starts from a collective effect of numerous well-tuned physical-chemical nanoscale properties as later it will become apparent, the key point is the principle of dye-sensitization of large band-gap semiconductor electrodes. In the DSSC, sensitization dyeing is made by coating the internal surfaces of the porous TiO_2 electrode with special dye molecules tuned to absorb the incoming photons. (Hagfeldt & Grätzel 2000.)

6.1.2 Charge Separation

The charge separation in DSSCs is based on an electron transfer process from the dye molecule to TiO_2 and a hole transport process from the thereby oxidized dye to the electrolyte. The electron transfer mechanism is affected by the electronic structure of the adsorbed dye molecule and the energy level between the excited state of the dye and the titanium dioxide conduction band. (Hagfeldt & Grätzel 1995.)

Furthermore, there are no significant macroscopic electric fields present between the individual nanoparticles in vast majority of the electrode. In this case, lack of band bending is a result of the individuality of all the nanocrystalline particles: If the film is ensemble, the sufficiently thick nanoparticle film could have a collective space charge. However, the electrolyte surrounding all the particles effectively decouples the particles and screens any existing electric fields to about a nanometer maximum. (Pichot & Gregg 2000b.)

6.1.3 Charge collection

In the DSSCs charge transport happens by electron transport in the nanostructured TiO_2 electrode and hole transport in the electrolyte as I_3^- . Both

charge transport mechanisms are equally important for the operation of the solar cell. (Hagfeldt & Grätzel 2000.)

[Ion transport in the redox electrolyte](#)

Usually the electrolyte in the DSSCs is an organic solvent which contains the redoxes pair I^-/I_3^- . In this case, it works as a hole-conducting medium. At the TiO_2 electrode the oxidized dye, left behind by the electron injected to the TiO_2 , is regenerated by I^- in the electrolyte in the reaction:



While, oppositely, electrode I_3^- is reduced to I^- in the reaction:



I_3^- is produced at the TiO_2 electrode and consumed at the counter-electrode, thus diffused across the electrolyte correspondingly. Because of this, I_3^- is often labeled as the hole carrier to draw similarities with the conventional pn-junction solar cells. Similarly, I^- is produced at the counter-electrode and diffused to the opposite direction in the electrolyte. This redox reaction in the electrolyte is a two-electron reaction (Ferber et al. 1998):



Which is composed of series of successive reactions:

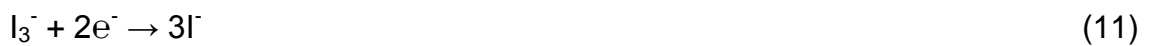




Recombination of the generated electrons with holes in the dye-sensitized nanostructured TiO₂ electrode can happen either after the electron injection or during its migration in the TiO₂ electrode on its way to the electrical back contact. (Zaban et al. 1997.)

In the dye-sensitized TiO₂ electrode, there is on the contrary vast amount of particle boundaries and a huge surface to volume ratio. However, the dye solar cell has no recombination losses at the grain boundaries at all. The reason is only electrons are transported through the semiconductor particles, while holes (oxidized ions) are carried by the electrolyte. So, the dye cell works as a majority carrier device, which is similar to a metal-semiconductor junction or a Schottky diode. (Green 1982, p. 175.)

According to Huang et al. (1997) the net recombination reaction at the TiO₂ - electrolyte interface is a two electron reaction:



Composed of sub-reactions



The reaction equation (13) shows that the actual electron acceptor in the recombination reaction is I_2 . The last equation is a slow dismutation reaction and rate limiting in the net recombination reaction.

7 PERFORMANCE AND APPLICATION OF TiO₂ DYED SOLAR CELL

7.1 Energy Conversion Efficiency

The high energy conversion efficiencies performed by the dye-sensitized solar cells are one important reason for DSSC research. As we can see from table 7.1, the Grätzel's group reported the highest efficiencies (Green 2001, Grätzel 2000, Nazeeruddin et al. 1993, O'Regan & Grätzel 1991):

Table 7.1 Some of the best or otherwise interesting performance results from the dyesensitized nanostructured TiO₂ solar cells (laboratory scale) showing the used dye, the cell efficiency, the reported area of the cell and the used illumination in the efficiency measurement. (Halme 2002)

Semi-conductor	Dye	η (%)	area (cm ²)	illumination (mW/cm ²)	reference
TiO ₂	?	11	0.25	100 (AM1.5)	Green 2001
TiO ₂	Black Dye	10.4	?	100 (AM1.5)	Grätzel 2000
TiO ₂	N3	10.0	0.3	96 (AM1.5)	Nazeeruddin et al. 1993
TiO ₂	N719 ²²	9.2	1.5	? (AM1.5)	Deb et al. 1998
TiO ₂	RuL ₂ (μ -(CN)Ru(CN)L'' ₂) ₂	7.1	0.5	75 (AM1.5)	O'Regan & Grätzel 1991
		7.9		8 (AM 1.5)	
TiO ₂	N3	6	1	100 (ELH lamp)	Hagfeldt et al. 1994
		7.3		11.5 (ELH lamp)	
TiO ₂	A Ru -phenantroline derivative	6.1	0.44	100 (AM 1.5)	Yanagida et al. 2000
TiO ₂	a coumarin derivative	5.6	?	100 (AM1.5)	Hara et al. 2001a
TiO ₂	Cu-2- α -oxymesoisochlorin	2.6	0.5	100 ("white light")	Kay & Grätzel 1993
TiO ₂	A natural cyanin-dye	0.56	0.9	100 (AM1.5)	Cherepy et al. 1997

L = 2,2'-bipyridyl-4,4'-dicarboxylic

L'' = 2,2'-bipyridine



An efficient charge transfer sensitizer dye is a prerequisite for high efficiency in the DSSCs. But at the same time, the dye developed by the Grätzel group is the most advanced. Natural dyes extracted from berries have been demonstrated in DSSCs with 0.56% cell efficiency (Cherepy et al. 1997).

Table 7.2 shows the purpose of replacing titanium dioxide with some other large band-gap semiconductor, such as $\text{In}_2\text{S}_3/\text{In}_2\text{O}_3$ (Hara et al. 2000b), SnO_2 (Fungo et al. 2000), ZnO (Bedja et al. 1997, Rensmo et al. 1997, Hara et al. 2000a), Nb_2O_5 (Sayama et al. 1998), CdS and CdSe (Hodes et al. 1992), but this replacement is not very successful yet.

Table 7.2 Some results reported using other semiconductors than TiO_2 in the DSSC showing the used dye, the cell efficiency, the reported area of the cell and the used illumination in the efficiency measurement. (Halme 2002)

Semi-conductor	Dye	η (%)	area (cm^2)	illumination (mW/cm^2)	reference
SnO_2/ZnO	N3	8	1.9	90 ("direct sunlight")	Tennakone et al. 1999
		15		10 ("diffuse daylight")	
ZnO	mercurochrome	2.5	0.09	100 (AM1.5)	Hara et al. 2000a
		1.4	0.25		
Nb_2O_5	N3	2	0.5	100 (AM1.5)	Sayama et al. 1998
ZnO	N3	2	0.25	56 ("solar simulator")	Rensmo et al. 1997

7.2 Long Term Stability

The stability of the dye-sensitized solar cells depends greatly on the designed chemical composition and the materials of the cell. Those unwanted impurities which are possibly included during the preparation of the cells affect stability of dye-sensitized solar cell too.

Table 7.3 Degradation factors and their effects on the cell performance. (Halme 2002)

Temperature	Visible light soaking	UV exposure
Stable power in over 2000 h in the dark at 60°C with purified propionitrile (Hinsch et al. 2001a).	Stable I_{sc} in over 4000 h at 45 °C and 1000W/m ² (Meyer et al. 2001).	Unstable efficiency with 26% decrease after UV dose in 960 h equivalent to 5 years outdoor exposure (Meyer et al. 2001).
30% decrease in efficiency after 875 h at 85°C with glass frit sealing (Hinsch et al. 2001a).	Stability depends on solvent:	UV shielding effect by additives such as MgI ₂ and CaI ₂ (Hinsch et al. 2001a).
Methoxyacetonitrile unstable above 45°C (Hinsch et al. 2001a).	methoxyacetonitrile unstable, propionitrile more stable with 15% decrease in efficiency after 3400h 1 sun at 45°C (Hinsch et al. 2001a).	Also partial recovery of the cell performance observed after UV treatment (Meyer et al. 2001).
Instability in thermal cycling test with acetonitrile as solvent (Hinsch et al. 2001b)		

Stable means here roughly: "no significant permanent decrease in performance observed". As we can see from Table 7.3, visible light soaking with no or little UV does not affect the cell performance. UV light has a long term effect of the cell performance, but adding efficient chemicals such as MgI₂ can reduce this effect significantly. On the other hand, thermal stability can be obtained by choosing the electrolyte solvent correctly (e.g. purified propionitrile).

Certain chemicals can enhance the stability of the cells. Especially 4-tertbutylpyridine (TBP) was found to increase the tolerance towards water in the electrolyte (Rijnberg et al. 1998), MgI₂ and CaI₂ increased the tolerance towards UV light (Hinsch et al. 2001a). Pure nitrile based solvents such as acetonitrile and propionitrile were the most stable solvents we have found now. According to research and experience, the importance of high chemical purity of the solvent and inert handling should be emphasized (Hinsch et al. 2001a).

8 SUMMARY

Coating improves the printing properties of paper and provides coated paper and paperboard enhanced smoothness, better ink receptivity, more whiteness, and more gloss.

Volume fraction of coating pigment is important. The smaller the particle size is, the glossier will be the coating. Yet there are still other pigment properties that an ideal pigment should have, titanium dioxide matches many of them.

As a commonly used coating pigment in paper industry, titanium dioxide pigments, TiO_2 pigments have very high refractive indices, whiteness, and high reflectance in the visible region of light and optimal particle size. These properties make them the most efficient white pigments. And titanium dioxide is also the most stable pigment; this is one important reason why titanium dioxide can be used in making dye solar cell.

Sustainable and renewable generation of energy/electricity by photovoltaic systems is being developed; solar electricity energy technology is a hot spot today. Solar cell producing electricity directly from solar radiation, is near the ideal way to use natural renewable energy. In the future, grid connected PV system power generation might be widely used, thus, the cost of solar electricity needs to be reduced.

The application of titanium dioxide solar cell requires only a low power output. Less stringent efficiency requirements of titanium dioxide solar cell make the manufacturing process more flexible, thus reducing manufacturing costs. Lower manufacturing costs and more flexibility in manufacturing process open the way for alternative production processes.

Because of its high efficiency, low manufacturing cost and long term stability, titanium dioxide is an ideal new material for solar electricity industry.

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